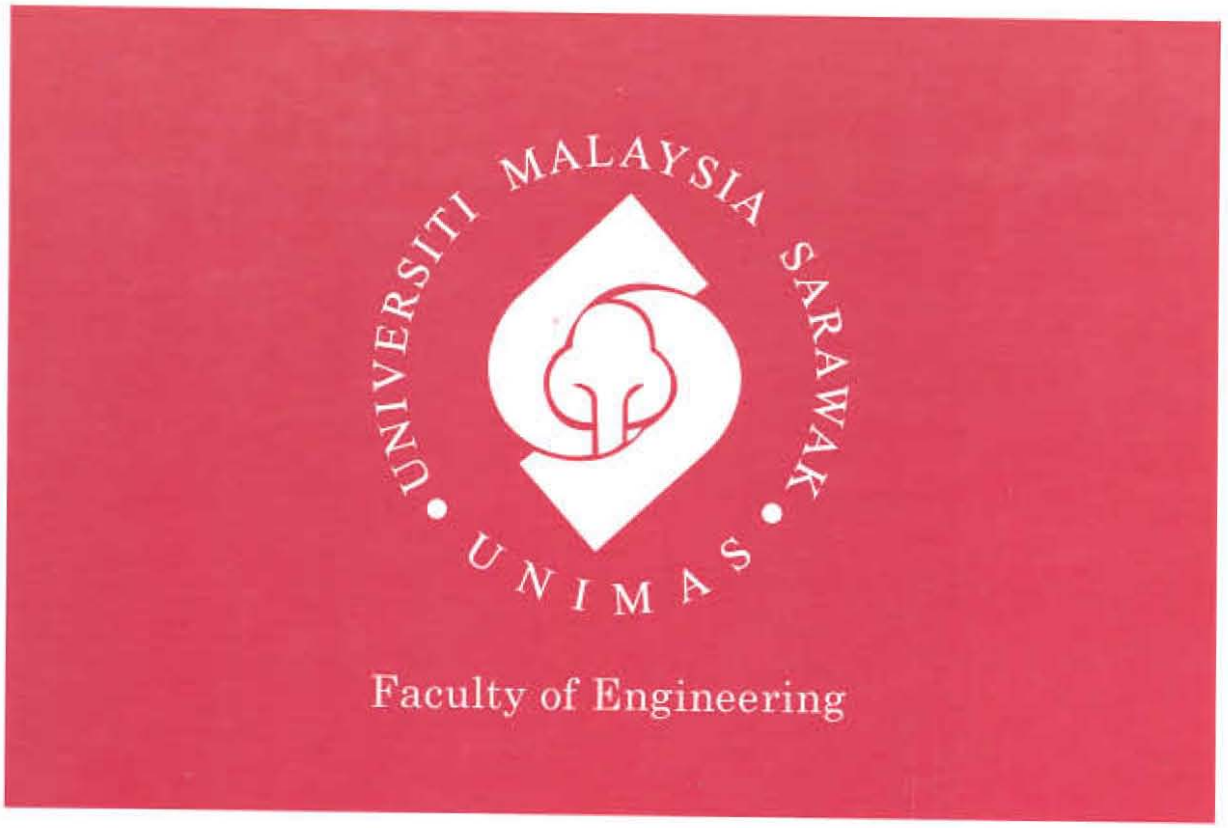

CHARACTERIZATION OF PLA-BASED NANOCOMPOSITES IN BIOMEDICAL APPLICATIONS

Yong Hui Sun

Bachelor of Engineering with Honours
(Chemical Engineering)
2015

UNIVERSITI MALAYSIA SARAWAK

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31st July 2015
(Date)

CHARACTERIZATION OF PLA-BASED NANOCOMPOSITES IN BIOMEDICAL APPLICATIONS

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Dissertation submitted in partial fulfilment of the requirement

For the Degree of

Bachelor of Engineering with Honours

(Chemical Engineering)

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Dedicated to my beloved parents and family, who always bestow me with full supports and encouragement

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ABSTRACT

The research aims to study the enhancement and improvement in the properties of PLA-based nanocomposites by adding different nanofillers at different weight percentages. Biodegradable polymers could be the most promising alternatives for replacing conventional petroleum-based polymers. Poly (lactic acid) can be derived from renewable resources and many researches had been carried out for the PLA-based nanocomposites. PLA-based nanocomposites is widely used in many applications such as biomedical applications. Nanocomposites used in biomedical applications requires specific requirements and limitations in pure PLA matrix such as lower thermal resistance and poor mechanical properties which can be enhanced by the incorporation of nanofillers such as nanoclays and fumed silica. Four different types of nanoclays were used in this study which were Nanomer® 1.28E, Nanomer® 1.30E, Nanomer® 1.31PS and Nanomer®1.34TCN . Fumed silica was used for the preparation of nanocomposites. The nanocomposites were prepared in different weight percentages of nanofillers by solvent casting method. The addition of nanofillers showed improvement in properties and characteristics of the PLA-based nanocomposites. The morphological study, mechanical properties, FTIR analysis, and BET surface area analysis were carried out and the results showed that the PLA/ fumed silica with 1.25wt% silica content was the best reinforcing agent with the largest surface area with . The mechanical properties of PLA-based nanocomposites showed that Nanomer® 1.31PS exhibited higher tensile strength and Young's modulus due to the strong dispersion and interaction between PLA matrix and nanoclays. The SEM analysis showed that Nanomer® 1.31PS acted as compatibilizer for reinforcing the interfacial action and miscibility between two phases. Potential interaction of PLA matrix and nanofillers was studied by FTIR analysis. PLA-based nanocomposites have promising potential that can be developed as future material in 21st century.

Keywords Biodegradable polymer; Poly (Lactic acid); Nanocomposites; Nanofillers; Nanoclays; Fumed Silica

ABSTRAK

Kajian ini bertujuan untuk mengkaji penambahbaikan dan peningkatan dalam sifat-sifat nanokomposit berbasis PLA dengan penambahan "nanofillers" yang berbeza mengikut peratusan berat yang berlainan. Polimer biodegradable boleh menjadi alternatif yang paling menjanjikan untuk menggantikan polimer konvensional yang berasaskan petroleum.Poli (laktik asid) dapat diperolehi daripada sumber yang boleh diperbaharui dan banyak kajian telah dijalankan bagi nanokomposit berbasis PLA. Nanokomposit berbasis PLA telah digunakan secara meluas dalam pelbagai aplikasi seperti aplikasi bioperubatan. Nanokomposit yang digunakan dalam aplikasi bioperubatan memerlukan syarat-syarat tertentu dan kekurangan dalam matrik PLA yang tulen seperti rintangan haba yang rendah dan sifat mekanikal yang tidak memuaskan boleh dipertingkatkan dengan penggabungan "nanofillers" seperti "nanoclays" dan silika fumed ke dalam polimer matrik. Empat jenis "nanoclays" iaitu Nanomer ®1.28E,Nanomer ® Nanomer ®1.30E, Nanomer ® 1.31PS dan Nanomer ® 1.34TCN telah digunakan dalam kajian. Silika fumed telah digunakan untuk penyediaan nanokomposit. Nanokomposit telah disediakan dengan peratusan berat yang berlainan mengikut "nanofillers" melalui kaedah "solvent casting". Penambahan "nanofillers" menunjukkan penambahbaikan dalam sifat and ciri nanokomposit berbasis PLA. Kajian morfologi, sifat mechanikal, analisis FTIR, dan analisis permukaan BET telah dijalankan dan hasil telah menunjukkan PLA/silika fumed nanokomposit dengan 1.25 wt % of kandungan silika merupakan agent pengukuh yang lebih baik dengan kawasan permukaan yang paling luas. Sifat mekanikal untuk nanokomposit menunjukkan Nanomer® 1.31PS memberi kekuatan tarik dan Modulus Young yang tinggi disebabkan penyebaran yang kuat dan interaksi antara PLA matrik dan "nanoclays". Analisis SEM menunjukkan Nanomer® 1.31PS bertindak sebagai untuk mengukuhkan tindakan antara permukaan dan kelarutan campuran antara dua fasa. Potensi interaksi bagi matrik PLA dengan "nanofillers" telah dikaji dengan analisis FTIR. Nanokomposit berbasis PLA mempunyai potensi yang menjanjikan untuk membangun sebagai bahan masa depan dalam abad ke-21.

Keywords Polimer biodegradable; Poly (Laktik asid); Nanokomposit; "Nanofillers"; "Nanoclays"; Silika Fumed

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dynes	:	10 micronewtons
°C	:	degree celsius
fmol /msPa	:	femtomole per meter per second per pascal
g	:	gram
g/10 min	:	gram per 10 minutes
g/cm^3	:	gram per cubic centimetre
gl^{-1}	:	gram per litre
GPa	:	giga pascal
J/g	:	joules per gram
J/m	:	joules per meter
J/ml	:	joules per millilitre
K	:	kelvin
kN	:	kilo newton
kg/m^3	:	kilogram per cubic meter
kg/mol	:	kilogram per mole
m%	:	mass percent solutions
MPa	:	mega pascal
µm	:	micrometre
nm	:	nanometer
cm^{-1}	:	per centimetre
%	:	percentage
mol^{-1}	:	per mole

m^2/g	:	square meter per gram
m^2/mol	:	square meter per mol
TS	:	tensile strength
US$	:	US dollar
wt %	:	weight percentage
E_Y	:	Young's modulus

LIST OF ABBREVIATIONS

Al_2O_3	:	alumina
BET	:	brunauer-emmett-teller
CO_2	:	carbon dioxide
CNT	:	carbon nanotubes
CEC	:	cationic exchange capacity
CPN	:	clay/polymer nanocomposites
DSC	:	differential scanning calorimetry
DMTA	:	dynamic-mechanical thermal analysis
EG	:	expanded graphite
FTIR	:	fourier transform infrared spectroscopy
GRAS	:	generally recognized as safe
HDPE	:	*high-density polyethylene*
-OH	:	hydroxide group
HA	:	hydroxyl-apatite
PHV	:	hydroxyl-valerate
ISBM	:	injection stretch blow molded
LDH	:	*lactate dehydrogenase*
$-CH_3$	:	methyl group
MMT	:	montmorillonite
NF-MS	:	nanofibrous microspehres
DMA	:	n, n'-dimethyacetamide
NMR	:	nuclear magnetic resonance

OMLS	:	organically modified layered silicate
OMMT	:	organo-modified montmorillonite
phr	:	parts per hundred parts of resin
PHB	:	poly- 3- hydroxybutyrate
PA6	:	polyamide 6
PBS	:	polybutylene succinate
PBSA	:	poly (butylene succinate-co-adipate)
PCL	:	polycaprolactone
PC	:	polycarbonates
LLDPE	:	polyethylene
PE	:	polyethylene
PEG	:	polyethylene glycol
PGA	:	polyglycolic acid
PHA	:	polyhydroxyalkanoates
PLA	:	poly(lactic acid)
PLGA	:	*poly(lactic-co-glycolic acid)*
PMMA	:	poly (methyl methacrylate)
PNIPAM	:	poly(n-isopropylacrylamide)
PPS	:	*polyphenylene sulfide*
PP	:	polypropylene
TPO	:	polypropylene-elastomer
PS	:	polystyrene
PT	:	polythiophenes
PVA	:	poly (vinyl) alcohol
PVC	:	poly (vinyl chloride)

CHAPTER 1

RESEARCH INTRODUCTION

1.1 Background of Study

Nanotechnology has been discussed and many researches have been done by scientists, engineers and researchers. It has become one of the prominent fields in all technical disciplines for today's researches and developments. It can be defined as "technology at the nanoscale" (Ramsden, 2011). Nanotechnology is a field of applied sciences and technologies that involve the applications in nanoscale and understanding about properties and phenomena of nanomaterials and nanostructures. Due to the higher demands from mankind in term of finer and better products, nanotechnology has been introduced for the development of innovation for new advanced materials. The coming decades is estimated to be dominated by nanotechnology in which the practice of identification of new advanced materials will be deviated . This new advanced technology requires new materials with superior physical, chemical and mechanical properties to meet the satisfaction of consumers (Fulekar, 2010).

Nanostructured materials have been studied worldwide for the development of new advanced materials with at least one dimension falling in nanoscale. One of the applications for this advanced materials is nanocomposites (Wu et al., 2015). Nanostructures are the new materials and are modulated over the zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D). A variety of nanomaterials have been developed and introduced based on these different ranges of dimension. There are three types of nanofillers or nanoreinforcements and they are categorized based on their dimensions in polymer matrices (Thomas, & Stephen, 2010). The categories of nanofillers are classified according to their morphology, aspect ratio and geometry such as layered which is clays, spherical which is silica and acicular which are whiskers and carbon nanotubes (Bordes et al., 2009). These nanofillers interacted with polymer matric to form polymer nanocomposite materials.

The decrease in the size of fillers into nanoscale had made the non-bonding interactions between the nanoparticle surface and polymer segment in which the vicinity of particles become stronger. The nanofillers such as layered silicate clays, carbon nanotubes, nanofibers and silica nanoparticles that are added into polymer matrix composites greatly enhanced and improved the properties of overall composite materials due to the massive surface-to-volume ratio of nanoparticles (Bhattacharya et al., 2007). Nanoclays or layered silicates and nanosilica are the most promising nanofillers that could enhance the properties of nanocomposites. Many researches had been conducted for the improvement in the properties of nanocomposites with the addition of nanofillers (Bhattacharya et al., 2007).

Nanocomposites are multiphase structure materials in which the dimensions fall in nanometer range in at least one of the phases (Anandhan & Bandyopadhyay, 2011). These high performed materials exhibit special combinations in properties and design possibilities and considered as materials of 21st century. Three types of combination of nanocomposites are available which includes iso-dimensional nanoparticles with three nano dimensions, nanotubes or whiskers with two nano dimensions and polymer-layered crystal nanocomposites with one nano dimension (Jamshidian et al., 2010). Nowadays, nanocomposites give innovative technology and opportunities in business and being environmental-friendly in the market for engineering polymers and useful in applications such as packaging and biomedical. The development of compostable and biodegradable polymers as new generation of polymers has received much attentions (Lai et al., 2014). Thermoplastics, thermosets and elastomers are used in research on making of polymer nanocomposites. Aliphatic polyesters are the most promising biodegradable materials among the biodegradable polymers due to the characteristics on readily susceptible to biological (Mohapatra et al., 2012). A combination of nanomaterials with the polymer matrix have the inherited properties with high strength and stiffness and improves the damage tolerance of nanocomposite materials (Sahay et al., 2014). The addition of nanofillers to enhance the properties of nanocomposites had been the topic of researches recently. Fukushimet al. (2009) asserted that addition of nanoscale fillers had great potential for being excellent in properties to the polymer nanocomposites. Joseph et al. (2014) discovered that macro, micro and nanofillers were added in PLA matrix system showed enhancement in mechanical, barrier and thermal properties.

Thus, in this research, the highlight will be focused on the improvement and enhancement of PLA matrix with the addition of nanofillers including four different types of nanoclays and fumed silica. Different weight percentages of nanoclays and fumed silica were added in PLA matrix to form nanocomposites. The performance of nanocomposites will be investigated using several methods and technique with equipment available.

1.2 Problem Statement of Research

Waste disposal issue has urged the contributions of research in effort on the development of new advanced materials with the combination of environmental sustainability and biodegradability or compostability. The biodegradable polymers have potential in solving this environmental issue brought by non-biodegradable polymers. However, the properties of the biodegradable polymers need to be improved and the main limitations of biodegradable polymers in the applications are the poor thermal and mechanical resistance. Poly (lactic acid) (PLA) has existed for several decades and it is considered as versatile polymer that made from renewable agriculture materials. Out of all biodegradable polymers, PLA has properties with good appearance, high mechanical strength, low toxicity and good barrier properties. The properties need to be improved for PLA to optimize its ability in engineering and industrial applications such as biomedical applications. Studies showed that the blending of PLA matrix with nanofillers could improve its properties and reduce cost. Various nanofillers have been considered as reinforcing agents for PLA matrix in order to enhance and improve the properties and provide additional functionalities to the polymers.

Thus this research focused on developing new nanomaterials based on PLA polymer matrix. Biodegradable polymers such as PLA are especially as interest for applications such as packaging and biomedical application(Hapuarachchi, & Peijs, 2010). However, the properties are the main constraints for the engineering applications especially in biomedical applications. PLA has been used in biomedical applications such as surgical sutures, implants and drug delivery systems. Special attention for advanced research in the properties improvement of PLA is essential. This research aimed to study the outcome of the interaction of poly (lactic acid) matrix with nanoclays and fumed silica at different weight percentages.

Solvent casting method will be used in this research for the preparation of nanocomposite sample and different weight percentage or weight ratio of nanofillers will be added in the PLA matric. Different types of nanoclays are used to investigate the best combination of nanocomposite materials. The outcome of the study is justified by the study of morphology, mechanical properties, and structural properties of the nanocomposites.

1.3 Research Objectives

This research project was conducted and carried out based on specific objectives which include:

a. To investigate the morphology, mechanical, and structural properties of poly (lactic acid) based nanocomposites.
b. To study the effect of different weight ratio of nanoclays and fumed silica on the properties of nanocomposites.
c. To compare the properties of nanoclays-based nanocomposites with the fumed-silica based nanocomposites.

1.4 Scope of Study

The scope of the research project focused on the improvement in the properties of PLA-based nanocomposites that suitable in engineering applications such as biomedical applications. The potential biodegradable polymer used to produce nanocomposites in this research is poly (lactic acid) and the advantages of biodegradable polymers in various applications also will be discussed. The enhancements of properties of nanocomposites are investigated with suitable methodology. Solvent casting technique is used for preparation of nanocomposites.

The morphology, mechanical, and structural properties are studied by several tests and analysis. Different types of nanoclays are used in this study to find out which types of nanoclay shows good performance when interacted with PLA matrix. A study on the combination of PLA matrix with fumed silica is also carried out to study the

performance of nanocomposites. The results will be compared among the nanofillers used and the performance of the nanocomposites will be analyzed.

1.5 Expected Outcomes of Research

The adding of nanoclays and fumed silica in poly (lactic acid) matrix respectively in preparation of biodegradable nanocomposites will changed the morphology, mechanical properties, chemical structures and surface area of nanocomposites. Different weight percentage of the nanofillers shows different characteristics in PLA-based nanocomposites. The different types of nanoclays also show different properties in PLA/nanoclays nanocomposites. PLA/fumed silica nanocomposites perform better compared to PLA/Nanoclays nanocomposites.

1.6 Summary

This chapter discussed about the background of the research project. The use of nanotechnology had innovated new advance materials in nanoscale and will be future technology for innovation. The properties of nanocomposites with the use of PLA matrix should be enhanced in order to be applicable in many others precise applications such as biomedical applications. Thus, the addition of nanofillers such as nanoclays and fumed silica seem to be a potential solution for the enhancements. The potential improvement on the properties of PLA based nanocomposites is studied for this project. Therefore, the effect on the interaction of PLA matrix with nanoclays or fumed silica in different weight ratio will be carried out. The problems arisen and the objectives to solve the problems are also discussed in this chapter. The research will be carried out based on the problem statement, aim and objectives discussed. The nanocomposites will be prepared in this research and the properties will be tested by several methods and techniques.